



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

KURITA, Tomoharu et al.

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Examiner: Kevin R. Kruer

For: FLEXIBLE METAL-CLAD LAMINATE AND PROCESS FOR PREPARING
THE SAME

DECLARATION

Honorable Commissioner of Patents and Trademarks
Washington, D. C. 20231

SIR:

I, Tomoharu KURITA declare that:

1) I was born in 1963. I graduated in March, 1988 from Tokyo University of Agriculture and Technology, Faculty of Engineering, Department of Polymer Engineering.

2) I have been employed by Toyo Boseki Kabushiki Kaisya since 1988. Since 1988, I have been engaged in the designing of polyamide-imide resins and polyimide resins, and also in the development of flexible metal-clad laminate using such resins.

3) In order to demonstrate the advantage of the present invention and the difference between the present invention and the cited prior art references, the following experiments were carried out under my direction and supervision.

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Experiment 1

The purpose of this Experiment was to clarify the difference in the effects based on the comparison between a polyamide-imide resin disclosed in Ohmura et al. (US 4,377,652) and a polyamide-imide resin of the present application.

More specifically, a polyamide-imide resin (Run No. 1) shown in Table 1 of Ohmura et al. was synthesized and a flexible metal-clad laminate was prepared using this resin.

It was found that the resulting flexible metal-clad laminate did not undergo crosslinking in the 200°C for 30 minutes heat-treatment nor satisfy the requirements for radius of curvature of a curl as set forth in Claim 1 of the present invention in the 400°C for 30 minutes heat-treatment.

(a) Synthesis of the polyamide-imide resin (Run No. 1) shown in Table 1 of Ohmura et al.

324 g of m-phenylenediamine and 303 g of triethylamine were placed into a flask equipped with calcium chloride tube, and 5L of N,N'-dimethylacetamide (DMAC) was added to the resultant mixture to give a solution. Another solution separately prepared by dissolving 632 g of trimellitic anhydride chloride in 2.5L of DMAC was added to the obtained solution under vigorous stirring with a magnetic stirrer. The resultant mixture was stirred at room temperature (20°C) for 3 hours to give a polyamide-imide resin solution.

(b) Measurement of reduced viscosity of the obtained polyamide-

imide resin solution

The polyamide-imide resin solution obtained in (a) above was placed in 300 ml of water, and was stirred with a magnetic stirrer to separate the product. The solids thus obtained were filtered off and washed with water, and was then dried at 55°C under reduced pressure, giving a solid polyamide-imide resin. Subsequently, 0.05 g of the obtained polyamide-imide resin was dissolved in 10 ml of N,N-dimethylformamide. Thereafter, reduced viscosity of the obtained solution at 30°C was measured with an Ubbelohde's viscometer. It was found that the viscosity was 1.0 dl/g. Thus, it was confirmed that the polyamide-imide resin (Run No. 1) shown in Table 1 of Ohmura et al. was produced.

(c) Preparation of a flexible metal-clad laminate

(A) Predrying step

The resin solution obtained in (a) above was continuously applied to a copper foil with a knife coater, leaving a 1 cm lengthwise border on both edges (uncoated) in such a manner that the thickness of the resin layer after removing the solvent therefrom was 20 μm .

The copper foil used was rolled copper foils (trade name "BHY-02-BT", manufactured by JAPAN ENERGY CORPORATION) having a surface roughness Ra of 0.35 μm and a thickness of 18 μm .

Subsequently, the coated metal foil was continuously passed through a floating-type drying furnace which was 20 m long. The speed of the line was adjusted so that the predrying conditions (100°C \times 5 minutes) used in Examples of the instant

invention were attained.

(B) Winding step

The lengthwise edges of the coated surfaces of the thus obtained ribbon-shaped laminates were covered with glass cloth tape (1 cm in width and 200 μ m in thickness), and the laminates were wound on aluminum tubes (3 inches in diameter) with the coated surface facing outward.

(C) Heat-treating and solvent removing step

The rolls obtained in the above winding step were heat-treated. Sample A was subjected to the heat-treatment at 100°C for 3 hours, at 150°C for 2 hours, and then at 200°C for 30 minutes. Sample B was subjected to the heat-treatment at 100°C for 3 hours, at 150°C for 2 hours, at 200°C for 30 minutes, and further at 400°C for 30 minutes.

Flexible metal-clad laminates were thus prepared by the above-described steps.

(d) Method for evaluation of the flexible metal-clad laminates

(d-1) N-methyl-2-pyrrolidone-insoluble content

A flexible metal-clad laminate was immersed in ferric chloride at 40°C (concentration: 35% by weight) to etch and remove the metal foil therefrom. The obtained resin film was dissolved in N-methyl-2-pyrrolidone, giving a 0.5% by weight solution of the resin film layer in N-methyl-2-pyrrolidone. The solution was prepared using a 100 ml Erlenmeyer flask.

Subsequently, this solution was heat-treated at 100°C (by immersing the Erlenmeyer flask in an oil bath at 100°C) for 2 hours. The Erlenmeyer flask was cooled to room temperature.

The insolubles in the Erlenmeyer flask were collected by filtration using a glass filter (No. 3G-2) while being washed with 100 ml of N-methyl-2-pyrrolidone.

Thereafter, the glass filter with the insolubles was dried in vacuum at 200°C for 20 hours. The weight of the dried glass filter was measured. From this weight was subtracted the original weight of the glass filter which had been preliminarily measured, thereby determining the weight of the insolubles. The insoluble content was calculated from the weight of the insolubles (Mi) and the weight of the resin film (Mf) by the following equation.

$$\text{Insoluble content (\%)} = [Mi/Mf] \times 100 \quad (4)$$

where Mi represents the weight (g) of the insolubles, and Mf represents the weight (g) of the resin film.

(d-2) radius of curvature of a curl

As shown in Fig. 5, a flexible metal-clad laminate (sample size: 10 cm x 10 cm) obtained in (c) above was left in a free state (the state that weight is not applied in the direction of curling). The distance (R) between the ends 102 and 102' which do not lie in the vertical plane S due to curling of the sample 100 and the distance h between the vertical plane S and each of the ends 102 and 102' were measured. The radius of curvature r was calculated by the following equation.

$$\text{Radius of curvature (r)} = (h/2) + (1/8) \times (R^2/h)$$

(e) Results of evaluation of the flexible metal-clad laminates

Results are shown in the following Table I.

Table I

	Insoluble content(%)	Radius of curvature of a curl (cm)
Sample A	0	1.8
Sample B	100	3.2

The polyamide-imide resin (Run No.1) used in Example 1 of Ohmura et al. was evaluated by preparing a flexible metal-clad laminate in the same manner as in the instant invention. As is evident from Table I, sample A underwent no crosslinking reaction with a heat-treatment at 200°C. In contrast, sample B underwent crosslinking reaction with a heat-treatment at 400°C but showed excessive curling.

Experiment 2

The purpose of this Experiment is to measure dimensional change at 200°C of the flexible metal-clad laminates of Examples 9 through 12 of the present application to verify based on the measurement results that all the products of Examples 9 through 12 satisfy the requirements recited in Claim 1 of the present application.

(a) Synthesis of polyamide-imide resins

(a-1) Synthesis of resin B-1 (for the purpose of reproduction of Example 9)

Into a reaction vessel were placed 384 g of trimellitic

acid anhydride, 378 g (90 mol%) of 1,5-naphthalenediisocyanate, 50 g (10 mol%) of 4,4'-diphenylmethanediisocyanate, 2.5 g of potassium fluoride (manufactured by TOKYO KASEI KOGYO CO., LTD.) and 2 kg of N-methyl-2-pyrrolidone. The mixture was heated to 130°C over 1 hour, and further reacted at 130°C for 5 hours. The resulting polymer had an inherent viscosity of 1.7 dl/g and a glass transition temperature of 381°C.

(a-2) Synthesis of resin B-2 (for the purpose of reproduction of Example 10)

Into a reaction vessel were placed 384 g of trimellitic acid anhydride, 399 g (95 mol%) of 1,5-naphthalenediisocyanate, 25 g (5 mol%) of 4,4'-diphenylmethanediisocyanate, 2.5 g of potassium fluoride and 2kg of N-methyl-2-pyrrolidone. The mixture was heated to 100°C over 1 hour, and further reacted at 100°C for 5 hours. The resulting polymer had an inherent viscosity of 1.8 dl/g and a glass transition temperature of 390°C.

(a-3) Synthesis of resin B-3 (for the purpose of reproduction of Example 11)

Into a reaction vessel were placed 384 g of trimellitic acid anhydride, 210 g (50 mol%) of 1,5-naphthalenediisocyanate, 251 g (50 mol%) of 4,4'-diphenylmethanediisocyanate, 2.5 g of potassium fluoride and 1.5 kg of N-methyl-2-pyrrolidone. The mixture was heated to 150°C over 1 hour, and further reacted at 150°C for 5 hours. The resulting polymer had an inherent viscosity of 1.2 dl/g and a glass transition temperature of

367° C.

(a-4) Synthesis of resin A-1 (for the purpose of reproduction of Example 12)

Into a reaction vessel were placed 192 g of trimellitic acid anhydride, 251 g (95 mol%) of 3,3'-dimethyl-4,4'-biphenyldiisocyanate, 8.7 g (5 mol%) of 2,4-tolylene diisocyanate, 0.5 g of sodium methylate and 2.5 kg of N-methyl-2-pyrrolidone. The mixture was heated to 150°C over 1 hour, and further reacted at 150°C for 5 hours. The resulting polymer had an inherent viscosity of 1.7 dl/g and a glass transition temperature of 315°C.

(b) Preparation of flexible metal-clad laminates of Examples 9, 10, 11, and 12 of the present application

(A) Predrying step

Each resin solution obtained in (a) above was continuously applied to copper foil with a knife coater, leaving a 1 cm lengthwise border on both edges (uncoated) in such a manner that the thickness of the resin layer after removing the solvent therefrom was 20 µm.

The copper foil used was rolled copper foils (trade name "BHY-02-BT", manufactured by JAPAN ENERGY CORPORATION) having a surface roughness Ra of 0.35 µm and thickness of 18 µm.

Subsequently, the coated metal foil was continuously passed through a floating-type drying furnace which was 20 m long. The speed of the line was adjusted so that the predrying conditions (100°C × 5 minutes) used in Examples 9 to 12 of the

present invention were attained.

(B) Winding step

For reproducing Examples 9 to 11, glass cloth tape (1 cm in width and 300 μ m in thickness) was placed on the uncoated area at both lengthwise edges of the ribbon-shaped laminates. The laminates were wound on aluminum tubes (3 inches in diameter) with the coated surface facing outward.

For reproducing Example 12, both uncoated lengthwise edges of the ribbon-shaped laminate were covered with tape as shown in Fig. 3. The laminates were wound on an aluminum tube (3 inches in diameter) with the coated surface facing outward.

(C) Heat-treating and solvent removing step

Subsequently, the heat-treatment was conducted at 200°C for 30 hours (under reduced pressure) and at 300°C for 4 hours (nitrogen).

(c) Measurement of dimensional change

Thermal gradient dimensional change in the directions of MD and TD was determined according to IPC-FC241 (IPC-TM-650, 2.2.4 (c)) under the conditions of 200°C \times 30 minutes.

(d) Results of evaluation of the flexible metal-clad laminates

Results are shown in the following Table II.

Table II

	Thermal gradient dimensional change at 200°C (%)	
	Direction MD	Direction TD
Example 9	-0.034	-0.035
Example 10	-0.038	-0.055
Example 11	-0.038	-0.042
Example 12	-0.044	-0.051

As is evident from Table II above, the thermal gradient dimensional changes at 200°C of the flexible metal-clad laminates of Examples 9 through 12 are within the range of thermal gradient dimensional change recited in Claim 1 of the present application.

Experiment 3

The purpose of this Experiment was to verify that a polyamide-imide having a structure represented by general formula (2) did not undergo crosslinking by a heat-treatment at 200°C.

(a) Preparation process of a flexible metal-clad laminate

A flexible metal-clad laminate was obtained in the same manner as in the reproduction experiment of Example 9 described in Experiment 2 above, except that the heat-treating and solvent removing step was conducted at 200°C for 20 hours (under reduced pressure).

(b) Measurement of N-methyl-2-pyrrolidone insoluble content

The insoluble content of the resin film layer obtained in (a) above was measured following the procedure of Experiment 1 (d-1).

The resulting measurement was less than 1%.

(c) Summary

It was confirmed that the insoluble content of a polyamide-imide resin of a structural formula (2) does not exceed 1% by a heat-treatment at 200°C for 20 hours.

I, the undersigned, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: Feb. 25, 2004

Tomoharu Kurita

Tomoharu Kurita